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Conserving approximations in nonequilibrium Green function and density functional theory

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1. – Introduction

We give a brief overview of nonequilibrium Green function theory and some connections with time-dependent density functional theory (TDDFT). We will focus on how to obtain approximations that satisfy the conservation laws. The account given here is not meant to be comprehensive but tries to put in logical order the main arguments and results that are sometimes found scattered in the literature.

2. – Nonequilibrium Green function theory

2˙1. *The action functional.* – We will study a system of interacting electrons in a time-dependent external potential $v(\mathbf{r},t)$ and vector potential $\mathbf{A}(\mathbf{r},t)$, such that the single-particle part of the Hamiltonian is

$$h_0(\mathbf{r},t) = \frac{1}{2}\left[-i\nabla + \mathbf{A}(\mathbf{r},t)\right]^2 + v(\mathbf{r},t) - \mu. \tag{1}$$

We use atomic units $\hbar = m = e = 1$. In the following, we are mainly interested in systems that evolve from an equilibrium state at some time t_0, a choice which is reflected in the inclusion of the chemical potential μ in h_0. Most of the theory can be generalized to much more general initial conditions, but this is a topic that deserves a more thorough

discusssion [1, 2, 3]. The total Hamiltonian is written in second-quantization as

$$\hat{H}(t) = \int d\mathbf{x}\, \hat{\psi}^\dagger(\mathbf{x}) h_0(\mathbf{r},t)\hat{\psi}(\mathbf{x}) + \frac{1}{2}\int\int d\mathbf{x}_1 d\mathbf{x}_2\, \hat{\psi}^\dagger(\mathbf{x}_1)\hat{\psi}^\dagger(\mathbf{x}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\hat{\psi}(\mathbf{x}_2)\hat{\psi}(\mathbf{x}_1), \tag{2}$$

where we use the notation $\mathbf{x} = (\mathbf{r},\sigma)$ and $d\mathbf{x}$ denotes integration over $\mathbf{r}$ as well as a summation over the spin indices. We will now define an action which will be used as a generating functional for our observables. To motivate our definition we consider the expectation value of an operator $\hat{O}$ for the case that the system is initially in an equilibrium state before a certain time t_0. For $t < t_0$ the expectation value of operator $\hat{O}$ in the Schrödinger picture is then given by $\langle\hat{O}\rangle = \mathrm{Tr}\,\{\hat{\rho}\hat{O}\}$ where $\hat{\rho} = e^{-\beta\hat{H}_0}/\mathrm{Tr}\; e^{-\beta\hat{H}_0}$ is the density matrix and $\hat{H}_0$ is the time-independent Hamiltonian that describes the system before the perturbation is switched on. We further defined $\beta = 1/k_B T$ to be the inverse temperature, and the trace involves a summation over a complete set of states in the Hilbert space. After we switch on the field the expectation value becomes

$$\langle\hat{O}(t)\rangle = \mathrm{Tr}\;\left\{\hat{\rho}\hat{O}_H(t)\right\} \tag{3}$$

where $\hat{O}_H(t) = \hat{U}(t_0,t)\hat{O}(t)\hat{U}(t,t_0)$ is the operator in the Heisenberg picture. The evolution operator $\hat{U}$ of the system is defined as the solution to the equations

$$i\partial_t\hat{U}(t,t') = \hat{H}(t)\hat{U}(t,t') \qquad i\partial_{t'}\hat{U}(t,t') = -\hat{U}(t,t')\hat{H}(t') \tag{4}$$

with the boundary condition $\hat{U}(t,t) = 1$. The formal solution of Eq. (4) can be obtained by integration to yield $\hat{U}(t,t') = T\exp\left(-i\int_{t'}^{t} d\tau\hat{H}(\tau)\right)$. The operator $e^{-\beta\hat{H}_0}$ can now be regarded as an evolution operator in imaginary time, i.e. $\hat{U}(t_0 - i\beta, t_0) = e^{-\beta\hat{H}_0}$, if we define $\hat{H}(t)$ to be equal to $\hat{H}_0$ on the contour running straight from t_0 to $t_0 - i\beta$ in the complex time plane. We can therefore rewrite our expression for the expectation value as

$$\langle\hat{O}(t)\rangle = \frac{\mathrm{Tr}\;\left\{\hat{U}(t_0 - i\beta, t_0)\hat{U}(t_0,t)\,\hat{O}\,\hat{U}(t,t_0)\right\}}{\mathrm{Tr}\;\left\{\hat{U}(t_0 - i\beta, t_0)\right\}} \tag{5}$$

If we read the time arguments of the evolution operators in the numerator of this expression from left to right we may say that the system evolves from t_0 along the real time axis to t after which the operator $\hat{O}$ acts. Then the system evolves back along the real axis from time t to t_0 and finally parallel to the imaginary axis from t_0 to $t_0 - i\beta$. A corresponding contour is displayed in Fig. 1. This observation motivates us to define the following action functional (compare with the action functionals used in Refs.[4, 5])

$$S = -\ln\mathrm{Tr}\;\left\{\hat{U}(t_0 - i\beta, t_0)\right\}, \tag{6}$$

where we define the evolution operator on the contour as

$$\hat{U}(t_0 - i\beta, t_0) = T_C \exp(-i \int dt \hat{H}(t)). \tag{7}$$

Here the integral is taken on the contour and T_C denotes time-ordering along the contour of Fig.1. For instance, time t_1 in Fig. 1 is later than time t_2 on the contour. Let us now see how this functional can be used as a generating functional by making variations with respect to parameters in the Hamiltonian. To do this one needs to consider changes in $\hat{U}$ which are readily evaluated using Eq.(4). For instance, when we make a perturbation $\delta\hat{V}(t)$ in the Hamiltonian we have using Eq.(4)

$$i\partial_t \, \delta\hat{U}(t, t') = \delta\hat{V}(t)\hat{U}(t, t') + \hat{H}(t)\delta U(t, t') \tag{8}$$

with a similar differential equation with respect to t' and boundary condition $\delta\hat{U}(t, t) = 0$. The solution to this equation is given by

$$\delta\hat{U}(t, t') = -i \int_{t'}^{t} d\tau \hat{U}(t, \tau)\delta\hat{V}(\tau)U(\tau, t') \tag{9}$$

from which variations in the action can be calculated. For instance, if we choose $\delta\hat{V}(t) = \int d\mathbf{x}\delta v(\mathbf{x}t)\hat{n}(\mathbf{x})$ where $\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})$ is the density operator we obtain the expectation value of the density as $\langle\hat{n}(\mathbf{x}t)\rangle = i\delta S/\delta v(\mathbf{x}t)$. More general expectation values can be obtained if we, as a formal device, add a time-dependent, nonlocal perturbation $u(1, 2)$ to the exponent in Eq. (7) which in our final equations will be set to zero. We define [4]

$$\hat{U}(t_0 - i\beta, t_0) = T_C \exp\left[-i \int dt \, \hat{H}(t) - i \int d1 \int d2 \, \hat{\psi}^\dagger(\mathbf{x}_1)u(1, 2)\hat{\psi}(\mathbf{x}_2)\right] \tag{10}$$

where we used the compact notation $1 = (\mathbf{x}_1, t_1)$. We define the one-particle Green's function G as the functional derivative of S with respect to the nonlocal perturbation u, i.e.

$$\begin{aligned} G(1, 2) &= \left.\frac{\delta S}{\delta u(2, 1)}\right|_{u=0} = \frac{1}{i}\frac{\text{Tr}\,\left\{\hat{U}(t_0 - i\beta, t_0)T_C\left[\hat{\psi}_H(1)\hat{\psi}^\dagger_H(2)\right]\right\}}{\text{Tr}\,\left\{\hat{U}(t_0 - i\beta, t_0)\right\}} \\ &= -i\langle T_C[\hat{\psi}_H(1)\hat{\psi}^\dagger_H(2)]\rangle, \end{aligned} \tag{11}$$

This Green function is thus defined for time-arguments on the contour. Such contour Green functions were first introduced by Keldysh [6] and are often denoted as Keldysh Green functions [1, 7, 8]. Let us now illustrate the effect of contour ordering by considering the situation in Fig. 1. In the figure, t_1 is later on the contour than t_2 and hence $U(t_0 - i\beta, t_0)T_C[\hat{\psi}_H(1)\hat{\psi}^\dagger_H(2)] = U(t_0 - i\beta, t_1)\hat{\psi}(\mathbf{x}_1)U(t_1, t_2)\hat{\psi}^\dagger(\mathbf{x}_2)U(t_2, t_0)$. Let us now

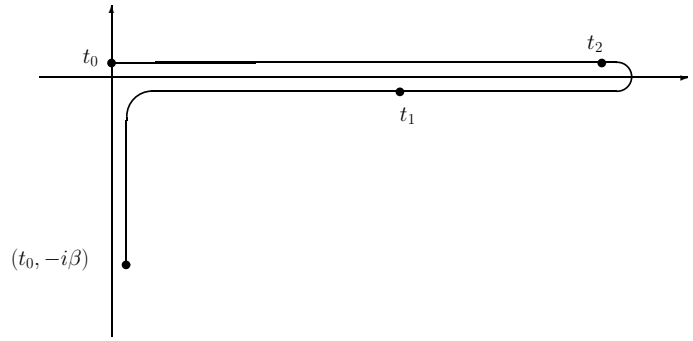

Fig. 1. – Keldysh contour. The forward and backward parts of the contour are on the real axis but are plotted slightly off this axis to display the two branches more clearly.

derive the boundary conditions that G satisfies. If we consider the Green function at $t_1 = t_0 - i\beta$ and use the cyclic property of the trace we find

$$G(\mathbf{x}_1 t_0 - i\beta, 2) = \frac{1}{i}\frac{\mathrm{Tr}\ \left\{\hat{\psi}(\mathbf{x}_1)\hat{U}(t_0 - i\beta, t_2)\hat{\psi}^\dagger(\mathbf{x}_2)\hat{U}(t_2, t_0)\right\}}{\mathrm{Tr}\ \left\{\hat{U}(t_0 - i\beta, t_0)\right\}}$$

$$= \frac{1}{i}\frac{\mathrm{Tr}\ \left\{\hat{U}(t_0 - i\beta, t_2)\hat{\psi}^\dagger(\mathbf{x}_2)\hat{U}(t_2, t_0)\hat{\psi}(\mathbf{x}_1)\right\}}{\mathrm{Tr}\ \left\{\hat{U}(t_0 - i\beta, t_0)\right\}} = -G(\mathbf{x}_1 t_0, 2). \tag{12}$$

The Green function defined in Eq. (11) therefore obeys the boundary condition $G(\mathbf{x}_1 t_0, 2) = -G(\mathbf{x}_1 t_0 - i\beta, t_2)$. The property $G(1, \mathbf{x}_2 t_0) = -G(1, \mathbf{x}_2 t_0 - i\beta)$ for the other argument is likewise easily verified. These boundary conditions are sometimes referred to as the Kubo-Martin-Schwinger conditions [9, 10, 2]. Similar boundary conditions are satisfied by the usual equilibrium temperature Green function which, in fact, is obtained for the special case where the time arguments are located on the contour along the imaginary axis t_0 to $t_0 - i\beta$, where the Hamiltonian is time-independent.

Higher-order Green functions can now be generated by higher-order differentiation of the action. For instance the second derivative of the action functional defines the linear transport coefficient L,

$$\left.\frac{\delta G(1,2)}{\delta u(4,3)}\right|_{u=0} = -G_2(1,3,4,2) + G(1,2)G(3,4) = -L(1,3,4,2), \tag{13}$$

where the two-particle Green function is defined according to

$$G_2(1,2,3,4) = \frac{1}{i^2}\frac{\mathrm{Tr}\ \left\{\hat{U}(t_0 - i\beta, t_0)T_C\left[\hat{\psi}_H(1)\hat{\psi}_H(2)\hat{\psi}^\dagger_H(3)\hat{\psi}^\dagger_H(4)\right]\right\}}{\mathrm{Tr}\ \left\{\hat{U}(t_0 - i\beta, t_0)\right\}}. \tag{14}$$

and satisfies similar boundary conditions as the one-particle Green function. The Green function G is a basic ingredient in a diagrammatic perturbation expansion and it directly gives us the expectation values of one-particle operators. For instance, if we denote by 1^+ the limit to t_1 from above on the contour, the density is quite simply

$$\langle \hat{n}(1) \rangle = -iG(1, 1^+) \tag{15}$$

and the current density is

$$\langle \mathbf{j}(1) \rangle = -i \left\{ \left[\frac{\nabla_1}{2i} - \frac{\nabla_{1'}}{2i} + \mathbf{A}(1) \right] G(1, 1') \right\}_{1'=1^+} \tag{16}$$

The calculated observables will obviously depend on what approximation scheme we use to obtain G. It is therefore important that these approximations are such that the calculated observables satisfy the macroscopic conservation laws, like e.g. the continuity equation, $\partial_t \langle \hat{n} \rangle = -\nabla \cdot \langle \mathbf{j} \rangle$. Such approximations are called *conserving approximations* and are the main topic of this presentation.

2˙2. *The Kadanoff-Baym equations.* – We now study the equation of motion for the Green function. For this purpose, we introduce the functions $G^>$ and $G^<$ according to

$$G^>(1, 1') = -i \langle \hat{\psi}_H(1) \hat{\psi}_H^\dagger(1') \rangle \tag{17}$$

$$G^<(1, 1') = i \langle \hat{\psi}_H^\dagger(1') \hat{\psi}_H(1) \rangle \tag{18}$$

such that we can write

$$G(1, 1') = \theta(t_1, t_{1'}) G^>(1, 1') + \theta(t_{1'}, t_1) G^<(1, 1'). \tag{19}$$

Here we use the step function θ generalized to arguments on the contour [1],

$$\theta(t_1, t_{1'}) = \begin{cases} 1 & \text{if } t_1 \text{ is later than } t_{1'} \text{ on the contour} \\ 0 & \text{otherwise} \end{cases} \tag{20}$$

Using the definition of operators in the Heisenberg picture, and the Hamiltonian as given in Eq. (2), the equation of motion for the annihilation operator is

$$\begin{aligned} i\partial_{t_1} \hat{\psi}_H(1) &= [\hat{\psi}_H(1), \hat{H}_H(t_1)] \\ &= \left[h_0(1) + \int d2\, \hat{\psi}_H^\dagger(2) w(2, 1) \hat{\psi}_H(2) \right] \hat{\psi}_H(1) \end{aligned} \tag{21}$$

where $w(1, 2) = \delta(t_1, t_2)/|\mathbf{r}_1 - \mathbf{r}_2|$ is the Coulomb interaction. The notation $\delta(t_1, t_2)$ again indicates that the time-arguments are on the contour. Using this equation one obtains

$$[i\partial_{t_1} - h_0(1)]\, G(1, 1') = \delta(1, 1') - i \int d2\, w(1, 2) G_2(1, 2, 2^+, 1'). \tag{22}$$

where $\delta(1,1') = \delta(\mathbf{x}_1 - \mathbf{x}_1')\delta(t_1, t_{1'})$. The problem is that the equation of motion for G depends on the two-particle Green function G_2. Instead of propagating the equation with some approximate form of G_2, we introduce the electronic self energy M, such that the term $-iG_2w$ is replaced with MG. If we introduce the inverse of the noninteracting Green function as $G_0^{-1}(1,2) = [i\partial_{t_1} - h_0(1)]\delta(1,2)$ the equation of motion becomes

$$\int d3\, G_0^{-1}(1,3)G(3,2) = \delta(1,2) + \int d3\, M(1,3)G(3,2). \tag{23}$$

Note that the integral over the t_3 variable goes along the entire contour. By multiplication with G from the left and G^{-1} from the right the adjoint equation

$$\int d3\, G(1,3)G_0^{-1}(3,2) = \delta(1,2) + \int d3\, G(1,3)M(3,2) \tag{24}$$

follows directly. The self-energy is a functional of the one-particle Green function, and as a consequence, Eqs. (23) and (24) constitute a set of equations that should be solved to self-consistency once the functional dependence of M on G is known. To generate a set of self-consistent equations we note that if we use Eq.(9) we can write Eq.(22) as [11]

$$[i\partial_{t_1} - h_0(1) - v_H(1)]\, G(1,1') = \delta(1,1') + i\int d2\, w(1^+,2)\frac{\delta G(1,1')}{\delta v(2)}. \tag{25}$$

where the potential v is the external potential in the single-particle part h_0 of the Hamiltonian and the Hartree potential v_H is defined as $v_H(1) = \int w(1,2)n(2)$. If we differentiate the definition of the inverse Green function

$$\int d3\, G^{-1}(1,3)G(3,2) = \delta(1,2) \tag{26}$$

with respect to v we obtain the identity

$$\int d3\, G^{-1}(1,3)\frac{\delta G(3,2)}{\delta v(4)} = -\int d3\, \frac{\delta G^{-1}(1,3)}{\delta v(4)}G(3,2) \tag{27}$$

If we solve this equation for $\delta G/\delta v$ we obtain

$$\frac{\delta G(1,2)}{\delta v(3)} = -\int d4d5\, G(1,4)\frac{\delta G^{-1}(4,5)}{\delta v(3)}G(5,2) \tag{28}$$

Note that if we add a function C to the rhs of Eq.(28) that satisfies $G^{-1}C = 0$ we obtain another solution to Eq.(27). However, since our system is initially in equilibrium we can deduce from the boundary conditions on G that C must be zero. For more general initial states C will be nonzero and account for initial correlations [8, 2, 3]. With Eq.(28) we see that we can write M as

$$M(1,2) = i\int d3d4\, G(1,3)w(1^+,4)\Gamma(32;4) - i\delta(1,2)\int d3\, w(1,3)G(3,3^+) \tag{29}$$

where we defined the vertex function Γ as

$$\Gamma(12;3) = -\frac{\delta G^{-1}(1,2)}{\delta v(3)} \tag{30}$$

Since $G^{-1} = G_0^{-1} - M$, Eq.(30) implies immediately that

$$\begin{aligned}\Gamma(12;3) &= \delta(1,2)\delta(1,3) + \int d4d5\, \frac{\delta M(1,2)}{\delta G(4,5)} \frac{\delta G(4,5)}{\delta v(3)} \\ &= \delta(1,2)\delta(1,3) + \int d4d5d6d7\, \frac{\delta M(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(67;3)\end{aligned} \tag{31}$$

We have therefore obtained the following set of self-consistent equations

$$0 = [i\partial_{t_1} - h_0(1)]\, G(1,1') - \delta(1,1') - \int d2\, M(1,2)G(2,1') \tag{32}$$

$$M(1,2) = i \int d3d4\, G(1,3)w(1^+,4)\Gamma(32;4) - i\delta(1,2) \int d3\, w(1,3)G(3,3^+) \tag{33}$$

$$\Gamma(12;3) = \delta(1,2)\delta(1,3) + \int d4d5d6d7\, \frac{\delta M(1,2)}{\delta G(4,5)} G(4,6)G(7,5)\Gamma(67;3) \tag{34}$$

These equations can now be iterated to obtain self-consistent equations for the Green function. For instance, if we take the simplest approximation for the vertex, namely $\Gamma(12;3) = \delta(1,2)\delta(1,3)$, and insert it into Eq.(33) we obtain

$$M(1,2) = iG(1,2)w(1^+,2) - i\delta(1,2) \int d3\, w(1,3)G(3,3^+) \tag{35}$$

This is the so-called Hartree-Fock approximation to M and will in the following be denoted as Σ^{HF}. By inserting this expression into Eq.(34) we obtain a new approximation for the vertex from which one can obtain a new self-energy. As one can readily convince oneself the time-local part (i.e. proportional to $\delta(t_1,t_2)$) of M is only given by Σ^{HF}. It is therefore convenient to single out the Hartree-Fock part of the self-energy, such that [1]

$$M(1,2) = \Sigma^{\rm HF}(1,2) + \theta(t_1,t_2)\Sigma^{>}(1,2) + \theta(t_2,t_1)\Sigma^{<}(1,2) \tag{36}$$

It will often also be convenient to extract only the Hartree potential from M. We will therefore define $\Sigma = M - v_H$. Using Eq.(36) we transform the contour integration to obtain:

$$\begin{aligned}&[i\partial_{t_1} - h_0(1)]\, G^{\lessgtr}(1,2) - \int d\mathbf{x}_3\, \Sigma^{\rm HF}(1,\mathbf{x}_3t_1)G^{\lessgtr}(\mathbf{x}_3t_1,2) = \\ &= \int_{t_0}^{t_1} d3\, \left[\Sigma^{>}(1,3) - \Sigma^{<}(1,3)\right] G^{\lessgtr}(3,2) - \int_{t_0}^{t_2} d3\, \Sigma^{\lessgtr}(1,2)\left[G^{>}(3,2) - G^{<}(3,2)\right] \\ &+ \int_{t_0}^{t_0-i\beta} d3\, G^{<}(1,3)\Sigma^{>}(3,2)\end{aligned} \tag{37}$$

The integration of the adjoint Eq. (24) can be done in exactly the same way, with the result

$$
\begin{aligned}
&[-i\partial_{t_2} - h_0^*(2)]\, G^{\lessgtr}(1,2) - \int d\mathbf{x}_3\, \Sigma^{\rm HF}(1,\mathbf{x}_3 t_2) G^{\lessgtr}(\mathbf{x}_3 t_1, 2) = \\
&= \int_{t_0}^{t_1} d3\, \left[G^{>}(1,3) - G^{<}(1,3)\right] \Sigma^{\lessgtr}(3,2) - \int_{t_0}^{t_2} d3\, G^{\lessgtr}(1,3) \left[\Sigma^{>}(3,2) - \Sigma^{<}(3,2)\right] \\
&+ \int_{t_0}^{t_0 - i\beta} d3\, G^{>}(1,3)\Sigma^{>}(3,2). \qquad (38)
\end{aligned}
$$

The Eqs. (37) and (38) are known as the Kadanoff-Baym equations [12, 2, 8]. For a given approximation of $\Sigma[G]$ these equations can solved by time-propagation. Since we have two first order equations in time one needs two conditions to determine the solution uniquely. These conditions are precisely the Kubo-Martin-Schwinger conditions derived above. In practice the equations are first solved on the contour from t_0 to $t_0 - i\beta$ parallel to the imaginary axis which amounts to a solution of the stationary problem. The functions such obtained can then be used as starting values for the real time propagation [13, 14, 15]

2˙3. *Conserving approximations.* – We will now discuss how to construct conserving approximations [16, 4]. We start from Eq.(13) and write

$$
\begin{aligned}
L(1,2,2',1') &= -\frac{\delta G(1,1')}{\delta u(2',2)} = \int d3d3'\, G(1,3)\frac{\delta G^{-1}(3,3')}{\delta u(2',2)} G(3',1') \\
&= -G(1,2')G(2,1') + \int d3d3'd4d4'\, G(1,3)\frac{\delta M(3,3')}{\delta G(4',4)} L(4',2,2',4) G(3',1') \\
&= L_0(1,2,2',1') - \int d3d3'd4d4'\, L_0(1,3',3,1')\gamma(3,4,4',3')L(4',2,2',4). \qquad (39)
\end{aligned}
$$

where $L_0(1,2,2',1') = -G(1,2')G(2,1')$ and $\gamma(1,2,2',1') = \delta M(1,1')/\delta u(2',2)$. Eq.(39) is known as the Bethe-Salpeter equation. Similarly as discussed in connection with Eqs.(27) and (28) an extra term C satisfying $G^{-1}C = 0$ may be added that accounts for initial correlations [2]. For equilibrium initial states the term again disappears. Defining the inverse of L, we can write Eq. (39) according to

$$
L^{-1}(1,2,2',1') = L_0^{-1}(1,2,2',1') + \gamma(2',1',1,2), \qquad (40)
$$

where $L_0^{-1}(1,2,2',1') = -G^{-1}(2',1)G^{-1}(1',2)$. Since L is symmetric under the interchange $(1,1') \leftrightarrow (2,2')$, the inverse function must have the same symmetry. This means that

$$
\gamma(2',1',1,2) = \frac{\delta M(2',2)}{\delta G(1,1')} = \frac{\delta M(1',1)}{\delta G(2,2')} = \gamma(1',2',2,1), \qquad (41)
$$

and we thus have a vanishing curl condition on M. Extracting the Hartree potential, $M = v_H + \Sigma$, we see that if the self-energy Σ is obtained from an underlying functional

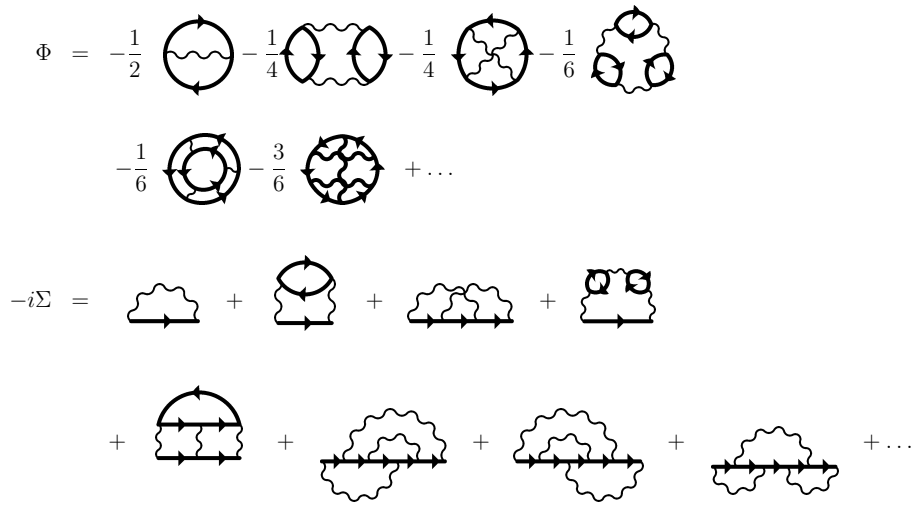

Fig. 2. – Some of the low-order Φ diagrams, and some of the self-energy diagrams obtained from $\Sigma = \delta\Phi/\delta G$. The prefactor of a Φ-diagram is $n_\Sigma/2n$ where n_Σ is the number of topologically different Σ-diagrams that can be generated from it and n is the number of interaction lines.

$\Phi[G]$, according to

$$\Sigma(1,2) = \frac{\delta\Phi}{\delta G(2,1)}, \tag{42}$$

then the function L^{-1} will automatically have the correct symmetry. Such a functional Φ can be constructed, as first shown by Luttinger and Ward [17], by summing over irreducible self-energy diagrams closed with an additional Green function line and multiplied by appropriate numerical factors,

$$\Phi[G] = \sum_{n,k} \frac{1}{2n} \int d1d2\, \Sigma_k^{(n)}(1,2) G(2,1^+) = \sum_{n,k} \frac{1}{2n} \mathrm{tr}\, \left[\Sigma_k^{(n)} G\right]. \tag{43}$$

The term n indicates the number of interaction lines and k labels Σ-diagrams. The trace tr indicates an integration over all variables (in contrast to the trace Tr that denotes a summation over a complete set of states in the Hilbert space). Some of the low-order diagrams are shown in Fig. 2, together with some of the corresponding self-energy diagrams. Baym [4] has proven the important result that when the self-energy is obtained from some approximate Φ-functional, the observables calculated from G satisfy the macroscopic conservation laws. We will describe his arguments for the number and momentum conservation laws. If we consider a perturbing potential corresponding to a gauge transformation $\mathbf{A} \to \mathbf{A} + \nabla\tilde{\Lambda}$, the single-particle Hamiltonian h_0 is changed to $h_0 = \frac{1}{2}[\nabla/i + \mathbf{A} + \nabla\tilde{\Lambda}]^2 + v + \partial_t\tilde{\Lambda}$. For an arbitrary $\tilde{\Lambda}$ with the boundary condition

$\tilde{\Lambda}(t_0) = \tilde{\Lambda}(t_0 - i\beta)$, it is then easily shown that the noninteracting Green function G_0 transforms according to

$$G_0(1,1';\tilde{\Lambda}) = e^{-i\tilde{\Lambda}(1)} G_0(1,1') e^{i\tilde{\Lambda}(1')}. \tag{44}$$

Due to the particle conservation at the vertices, it can be shown [4] that also Σ and G transform like G_0 in Eq. (44),

$$G(1,1';\tilde{\Lambda}) = e^{-i\tilde{\Lambda}(1)} G(1,1') e^{i\tilde{\Lambda}(1')}. \tag{45}$$

From this relation, we see that the first-order change in G due to $\tilde{\Lambda}$ is

$$\delta G(1,1') = -i \left[\tilde{\Lambda}(1) - \tilde{\Lambda}(1')\right] G(1,1'), \tag{46}$$

and the change in Φ, given by $\delta\Phi = \Sigma\delta G$, is then

$$\delta\Phi = i \int d1d1' \left[\Sigma(1',1)G(1,1') - \Sigma(1,1')G(1',1)\right] \tilde{\Lambda}(1). \tag{47}$$

Since there is one ingoing and one outgoing Green function at each vertex in the Φ diagrams, the exponential factors in Eq. (45) cancel, and the gauge transformation is hence an invariance of Φ. This is true for arbitrary $\tilde{\Lambda}$, and Eq. (47) thus leads to the equation

$$\int d1' \left[\Sigma(1,1')G(1',1) - G(1,1')\Sigma(1',1)\right] = 0. \tag{48}$$

Subtracting the equations of motion Eqs. (23), (24), $G_0^{-1}G - GG_0^{-1}$, we obtain

$$\begin{aligned} &[i\partial_{t_1} + i\partial_{t_2}]G(1,2) \\ &= [h_0(1) - h_0^*(2)]G(1,2) + \int d3 \left[G(1,3)M(3,2) - M(1,3)G(3,2)\right]. \end{aligned} \tag{49}$$

Taking the limit $t_2 \to t_1^+$ and using $n(1) = -iG(1,1^+)$ and Eq.(48), we finally obtain the result that for a Φ-derivable approximation the continuity equation

$$\partial_{t_1} \langle n(1)\rangle + \nabla_1 \cdot \langle \mathbf{j}(1)\rangle = 0. \tag{50}$$

is satisfied, where the current is given by Eq. (16).
Closely related to the number conservation are the so-called Ward-identities [18, 19]. To obtain them we study the changes in the Green function induced by a gauge transformation. For simplicity we will consider variations around $\mathbf{A} = 0$. If we define $\mathbf{j}(\mathbf{x}) = [\hat{\psi}^\dagger(\mathbf{x})\nabla\hat{\psi}(\mathbf{x}) - (\nabla\hat{\psi}^\dagger(\mathbf{x}))\hat{\psi}(\mathbf{x})]/2i$ the perturbing potential is given by

$$\delta\hat{V}(t_1) = \int d\mathbf{x}_1 (\hat{\mathbf{j}}(\mathbf{x}_1) \cdot \nabla_1 \tilde{\Lambda}(1) + \hat{n}(\mathbf{x}_1)\partial_{t_1}\tilde{\Lambda}(1)) \tag{51}$$

The change in $G(1,1')$ is therefore

$$(52)\int d2\left[\frac{\delta G(1,1')}{\delta v(2)}\partial_{t_2}\tilde{\Lambda}(2)+\sum_\mu\frac{\delta G(1,1')}{\delta A_\mu(2)}\nabla_{2,\mu}\tilde{\Lambda}(2)\right]=-i\left[\tilde{\Lambda}(1)-\tilde{\Lambda}(1')\right]G(1,1').$$

It will be convenient to denote the functional derivatives of G as Λ_0 and Λ_μ. For the exact systems these functions can be indentified with the following time-ordered products

$$\Lambda_0(11';2)=\frac{\delta G(1,1')}{\delta v(2)}=-\langle T_C[\hat{\psi}_H(1)\hat{\psi}^\dagger_H(1')\Delta\hat{n}(2)]\rangle \tag{53}$$

$$\Lambda_\mu(11';2)=\frac{\delta G(1,1')}{\delta A_\mu(2)}=-\langle T_C[\hat{\psi}_H(1)\hat{\psi}^\dagger_H(1')\Delta\hat{j}_\mu(2)]\rangle \tag{54}$$

where we used the notation $\Delta\hat{O}=\hat{O}-\langle\hat{O}\rangle$. These functions are closely related to the vertex and the density and current response functions. An integration by parts in Eq.(52) now leads to

$$(55)-\int d2\,\tilde{\Lambda}(2)\left\{\partial_{t_2}\Lambda_0(11';2)+\sum_\mu\nabla_\mu\Lambda_{2,\mu}(11';2)\right\}=-i\left[\tilde{\Lambda}(1)-\tilde{\Lambda}(1')\right]G(1,1'),$$

where we have used the boundary condition $\tilde{\Lambda}(t_0)=\tilde{\Lambda}(t_0-i\beta)$. Demanding that this equation is satisfied for arbitrary $\tilde{\Lambda}$, we obtain

$$\frac{\partial}{\partial t_2}\Lambda_0(11';2)+\sum_\mu\nabla_{2,\mu}\Lambda_\mu(11';2)=i\left[\delta(1,2)-\delta(1',2)\right]G(1,1'). \tag{56}$$

This equation is in fact the generalized Ward identity which relates the vertex and the self-energy. This equation can be made more explicit by defining the generalized vertex functions

$$\Gamma_0(11';2)=-\frac{\delta G^{-1}(1,1')}{\delta v(2)} \tag{57}$$

$$\Gamma_\mu(11';2)=-\frac{\delta G^{-1}(1,1')}{\delta A_\mu(2)} \tag{58}$$

The function Γ_0 is the same vertex that we already introduced in Eq.(30) and which satisfies Eq.(34) if G is solved from an equation of motion with a given $\Sigma[G]$. Using Eq.(28) we see that for $i=0\ldots4$ the functions Λ_i are related to the vertex functions Γ_i by

$$\Lambda_i(11';2)=-\int d3d4\,G(1,3)G(4,1')\Gamma_i(34;2). \tag{59}$$

With $\mathbf{\Lambda}$ on this form, Eq. (56) yields an equation of motion for $\mathbf{\Gamma}$,

$$\partial_{t_2}\Gamma_0(11';2)+\sum_\mu \nabla_{2,\mu}\Gamma_\mu(11';2)=-i\left[\delta(1',2)-\delta(1,2)\right]G^{-1}(1,1'). \tag{60}$$

Since $G^{-1}=G_0^{-1}-M$ this equation relates the vertex and the self-energy and is known as the generalized Ward identity [19]. The significance of the Ward identity is that it implies gauge invariance and an important sum rule for the response functions. To see this we define the following matrix of density and current response functions

$$\chi_{ij}(1,2)=-i\langle T_C[\Delta\hat{j}_i(1)\Delta\hat{j}_j(2)]\rangle \tag{61}$$

where $i,j=0\ldots4$ and we define $\hat{j}_0=\hat{n}$. These functions can be obtained from the equal time limit $1'\to 1^+$ of the functions $\Lambda_i(11';2)$ since $\langle T_C[\Delta\hat{j}_i(1)\Delta\hat{j}_j(2)]\rangle = \langle T_C[\hat{j}_i(1)\Delta\hat{j}_j(2)]\rangle$. Then taking the limit $1'\to 1^+$ in Eq.(56) gives

$$\partial_{t_2}\chi_{00}(1,2)+\sum_\mu \nabla_{2,\mu}\chi_{0\mu}(1,2)=0. \tag{62}$$

If we on the other hand apply the operator $(\nabla_1-\nabla_{1'})/2i$ to Eq.(56) and then set $1'=1^+$ we find

$$\partial_{t_2}\chi_{\mu 0}(1,2)+\sum_\nu \nabla_{2,\nu}\chi_{\mu\nu}(1,2)=-n(1)\nabla_{1,\mu}\delta(1,2) \tag{63}$$

Now the response functions χ_{ij} have the structure

$$\chi_{ij}(1,2)=\theta(t_1,t_2)\chi^{>}_{ij}(1,2)+\theta(t_2,t_1)\chi^{<}_{ij}(1,2) \tag{64}$$

If we insert this expression into Eq.(62) and Eq.(63) we obtain the equations

$$\chi^{>}_{00}(\mathbf{r}_1t,\mathbf{r}_2t)-\chi^{<}_{00}(\mathbf{r}_1t,\mathbf{r}_2t)=0 \tag{65}$$

$$\chi^{>}_{\mu 0}(\mathbf{r}_1t,\mathbf{r}_2t)-\chi^{<}_{\mu 0}(\mathbf{r}_1t,\mathbf{r}_2t)=-n(\mathbf{r}_1t)\nabla_{1,\mu}\delta(\mathbf{r}_1-\mathbf{r}_2) \tag{66}$$

$$\partial_{t_2}\chi^{\lessgtr}_{00}(1,2)+\sum_\mu \nabla_{2,\mu}\chi^{\lessgtr}_{0\mu}(1,2)=0 \tag{67}$$

$$\partial_{t_2}\chi^{\lessgtr}_{\mu 0}(1,2)+\sum_\nu \nabla_{2,\nu}\chi^{\lessgtr}_{\mu\nu}(1,2)=0 \tag{68}$$

Eqs.(67) and (68) are gauge conditions on the response functions and guarantee that pure gauges do not introduce density or current changes in the system. Eq.(66) is equivalent to the commutator [20]

$$\langle[\hat{j}_\mu(\mathbf{r}_1t),\hat{n}(\mathbf{r}_2t)]\rangle=-in(\mathbf{r}_1t)\nabla_{1,\mu}\delta(\mathbf{r}_1-\mathbf{r}_2)=i\nabla_{2,\mu}[n(\mathbf{r}_1t)\delta(\mathbf{r}_1-\mathbf{r}_2)] \tag{69}$$

which is for the exact system also easily verified by direct evaluation. Now a combination of Eq.(66) and Eq.(67) leads to a famous sum rule for the density-density response function. We have

$$\partial_{t_2}(\chi^{>}_{00}(1,2)-\chi^{<}_{00}(1,2))|_{t_1=t_2} = -\sum_\mu \nabla_{2,\mu}(\chi^{>}_{0\mu}(1,2)-\chi^{<}_{0\mu}(1,2))|_{t_1=t_2}$$

$$= \sum_\mu \nabla_{2,\mu}(\chi^{>}_{\mu 0}(2,1)-\chi^{<}_{\mu 0}(2,1))|_{t_1=t_2} = \sum_\mu \nabla_{2,\mu}\nabla_{1,\mu}(n(\mathbf{r}_2 t_1)\delta(\mathbf{r}_1-\mathbf{r}_2)) \tag{70}$$

If we consider the case that we perturb the system from an equilibrium state then the unperturbed density $n_0(\mathbf{r})$ is time-independent and the response functions depend on $t_1 - t_2$ and can be Fourier transformed with respect to $t_1 - t_2$. We define the retarded response function as

$$\chi_{00,R}(1,2) = \theta(t_1-t_2)(\chi^{>}_{00}(1,2)-\chi^{<}_{00}(1,2)) \tag{71}$$

where θ is the usual Heaviside function (i.e. not the contour one). Then Eq.(70) implies (see Appendix) in frequency space that

$$\int_{-\infty}^{+\infty} d\omega\, \omega \chi_{00,R}(\mathbf{r}_1,\mathbf{r}_2;\omega) = -i\pi \sum_\mu \nabla_{2,\mu}\nabla_{1,\mu}(n_0(\mathbf{r}_2)\delta(\mathbf{r}_1-\mathbf{r}_2)) \tag{72}$$

This equation is known as the frequency or f-sum rule. Satisfaction of this sumrule has been checked numerically by Kwong and Bonitz [21]. They solved for the electron gas the Kadanoff-Baym equations for a conserving approximation in the presence of a time-dependent field and calculated the changes in G. By dividing out the applied field, which amounts to taking the derivative $\delta G/\delta v$, they obtained the response function. The f-sum rule was found to be satisfied to high numerical accuracy. This technique has also the important practical advantage that it avoids solving a complicated equation for the vertex.

2˙4. *Momentum conservation.* – To derive the momentum conservation law we follow Baym [4] and consider a system as viewed by a moving observer at postion $\mathbf{r}' = \mathbf{r} - \mathbf{R}(t)$. with the boundary condition $\mathbf{R}(t_0) = \mathbf{R}(t_0 - i\beta)$. The one-body part of the Hamiltonian as viewed from a moving frame is then given by

$$\tilde{h}_0(\mathbf{r}'t;\mathbf{R}) = -\frac{1}{2}(-i\nabla' + \mathbf{A}(\mathbf{r}'+\mathbf{R}(t),t))^2 + i\partial_t \mathbf{R}(t)\cdot\nabla' + v(\mathbf{r}'+\mathbf{R}(t),t) \tag{73}$$

In the moving frame the solution for the equation of motion for G_0

$$(i\partial_t - \tilde{h}_0(1;\mathbf{R}))G_0(1,1';\mathbf{R}) = \delta(1,1') \tag{74}$$

is given by

$$G_0(\mathbf{r}_1 t_1, \mathbf{r}_1' t_1';\mathbf{R}) = G_0(\mathbf{r}_1 + \mathbf{R}(t_1), t_1, \mathbf{r}_1' + \mathbf{R}(t_1'), t_1';\mathbf{R}=0) \tag{75}$$

as can be directly checked by insertion into the equation of motion and verification of the boundary conditions. The same transformation law applies to G. This follows immediately from a diagrammatic expansion of G since the Coulomb interaction is local in time and depends only on the difference between the spatial coordinates and therefore the integrals over all space at the vertices are not changed by a shift in the origin. For the same reason Φ is unchanged by the replacement $G \to G(\mathbf{R})$, and therefore $0 = \delta\Phi = \Sigma\delta G = \Sigma\nabla G \cdot \delta\mathbf{R}$ implies

$$\int d1' \left[\Sigma(1,1')\nabla_1 G(1',1) + \Sigma(1',1)\nabla_1 G(1,1')\right] = 0. \tag{76}$$

If we now apply the operator $\frac{1}{2}[\frac{\nabla_1}{i} + \mathbf{A}(1) - \frac{\nabla_{1'}}{i} + \mathbf{A}(1')]$ to Eq. (49), take $1' = 1^+$, and integrate over $\mathbf{x}_1$ we obtain using Eq.(76) (the details are somewhat tedious)

$$\frac{d}{dt}\langle\hat{\mathbf{P}}(t)\rangle = -\int d\mathbf{x}_1 \, \{\langle\hat{n}(1)\rangle\mathbf{E}(1) + \langle\mathbf{j}(1)\rangle \times \mathbf{B}\}\,. \tag{77}$$

where the electric field is $\mathbf{E}(1) = -\nabla_1 v(1) - \partial\mathbf{A}/\partial t$ and the magnetic field is $\mathbf{B} = \nabla \times \mathbf{A}$. The quantity $\mathbf{P}(t)$ is the total momentum given by $\langle\mathbf{P}(t_1)\rangle = \int d\mathbf{x}_1 \langle\mathbf{j}(1)\rangle$. We therefore obtain the result that Φ-derivable approximations obey the momentum conservation law Eq.(77). In a similar manner we can also derive the energy and angular momentum conservation laws by considering how the Green function and the Φ-functional transform under time-translations and rotations. The main steps can be found in Refs. [16, 4]

3. – Time-dependent density-functional theory

3˙1. *The Sham-Schlüter equation.* – We now make a connection with time-dependent density functional theory [22, 23]. Let us first consider a noninteracting system. To this noninteracting system there corresponds a Green function G_s with the equations of motion

$$(i\partial_{t_1} - h_s(1))G_s(1,2) = \delta(1,2) \tag{78}$$

$$(-i\partial_{t_2} - h_s^*(2))G_s(1,2) = \delta(1,2) \tag{79}$$

At $t = t_0$ the system is in its ground state. The system is then described by one-particle orbitals that satisfy.

$$h_s(\mathbf{x}t_0)\varphi_j(\mathbf{x}) = \epsilon_j\varphi_j(\mathbf{x}) \tag{80}$$

On the imaginary part of the contour where the Hamiltonian is time-independent the orbitals are given by $\phi_i(\mathbf{x}t) = \varphi_i(\mathbf{x})\exp(-i\epsilon_i(t-t_0))$. For real times we define the orbitals to be the solution of

$$(i\partial_t - h_s(\mathbf{x}t))\phi_j(\mathbf{x}t) = 0 \tag{81}$$

with boundary condition $\phi_i(\mathbf{x}t_0) = \varphi_i(\mathbf{x})$. If we further define $n_j = (e^{\beta\epsilon_j}+1)^{-1}$ then the Green function

$$G_s(1,2) = -i\theta(t_1,t_2)\sum_j \phi_j(1)\phi_j^*(2)(1-n_j) + i\theta(t_2,t_1)\sum_j \phi_j(1)\phi_j^*(2)n_j \tag{82}$$

satisfies the equations of motion Eq.(78) and Eq.(79), with the boundary conditions

$$G_s(\mathbf{x}_1 t_0 - i\beta, 2) = -G_s(\mathbf{x}_1 t_0, 2) \tag{83}$$

$$G_s(1, \mathbf{x}_2 t_0 - i\beta) = -G_s(1, \mathbf{x}_2 t_0). \tag{84}$$

Let us consider the case that we have no vector potentials and let h_s be of the form

$$h_s(\mathbf{x}t) = -\frac{\nabla^2}{2} + v_s(\mathbf{x}t) \tag{85}$$

where v_s is a local potential. In the following we will split v_s as follows

$$v_s(1) = v(1) + v_H(1) + v_{xc}(1) \tag{86}$$

which defines the exchange-correlation potential v_{xc}. Then

$$G(1,1') = G_s(1,1') + \int d2d3\, G_s(1,2)[\Sigma(2,3) - \delta(2,3)v_{xc}(2)]G(3,1') \tag{87}$$

is a solution of Eq.(32) with similar boundary conditions as in Eqs.(83) and Eq.(84) (remember that $M = \Sigma + v_H$). We note that for more general initial conditions extra terms will appear in the self-energy that take into account these initial correlations [2, 3]. We now require that the noninteracting system will have the same density as the interacting one. We therefore require $n(1) = -iG(1,1^+) = -iG_s(1,1^+)$ which together with Eq.(87) leads to the following integral equation for v_{xc}:

$$\int d2\, G_s(1,2)G(2,1)v_{xc}(2) = \int d2d3\, G_s(1,2)\Sigma(2,3)G(3,1). \tag{88}$$

This equation is known as the time-dependent Sham-Schlüter equation [25]. As shown by Runge and Gross [26] v_{xc} is a functional of the density and the initial state of the system. If an approximate form of this functional $v_{xc}[n]$ is given the one-particle equations Eq.(81) can be solved self-consistently. These equations are known as the Kohn-Sham equations of time-dependent density functional theory and the noninteracting system with the same density as the true system is known as the Kohn-Sham system [24]. Suppose now that Σ is a Φ-derivable approximation. Then the momentum calculated from the Green function satisfies Eq.(77), i.e.

$$\partial_{t_1}\langle \mathbf{P}(t_1)\rangle = \partial_{t_1}\int d\mathbf{x}_1\, \langle \mathbf{j}(1)\rangle = -\int d\mathbf{x}_1\, n(1)\nabla v(1). \tag{89}$$

Now with the help of the continuity equation (50) the momentum can also be written as $\mathbf{P}(t) = \int d\mathbf{x}\,\mathbf{r}\,\partial_t n(\mathbf{x}t)$. Since the Kohn-Sham system also has density $n(1)$ and obeys the same conservation law with v replaced by v_s we can readily derive that

$$\int d\mathbf{x}_1 n(1)\nabla_1 v_{xc}(1) = 0. \tag{90}$$

We have therefore proved the result that an exchange-correlation potential obtained from a Φ-derivable Σ in Eq.(88) does not apply a force to the system. If we take the functional derivative of this equation with respect to the density we obtain

$$\int d1\, f_{xc}(1,2)\nabla_1 n(1) = \nabla_2 v_{xc}(2). \tag{91}$$

where we defined the exchange-correlation kernel $f_{xc}(1,2) = \delta v_{xc}(1)/\delta n(2)$ that plays an important role in density-functional response theory [28]. The latter equation can also be derived in a different way. Eq.(87) can along the lines described above also be derived for an observer in a moving frame with position vector $\mathbf{R}(t)$. The transformation property Eq.(75) of the Green function together with Eq.(88) then leads to

$$v_{xc}([n(\mathbf{r}+\mathbf{R}(t))];\mathbf{r}t) = v_{xc}([n(\mathbf{r}t)];\mathbf{r}+\mathbf{R}(t),t). \tag{92}$$

The importance of this relation has been stressed by Vignale who also showed that it implies the so-called harmonic potential theorem [27]. Expansion of Eq.(92) in $\mathbf{R}$ again leads to Eq.(91) [27].
Let us now look at some approximate solutions of Eq.(87). A first iteration of Eq.(87) leads to

$$\tilde{G}(1,1') = G_s(1,1') + \int d2d3\, G_s(1,2)[\Sigma[G_s](2,3) - \delta(2,3)v_{xc}(2)]G_s(3,1'). \tag{93}$$

It is important to note that the Green function $\tilde{G}$ for a Φ-derivable $\Sigma = \delta\Phi[G_s]/\delta G_s$ where Σ is expressed in terms of G_s rather than G, also satisfies all conservation laws. This follows simply because G and G_s behave similarly under the transformations that we considered and all our previous derivations can be repeated. The Sham-Schlüter equation corresponding to Eq.(93) is given by

$$\int d2\, G_s(1,2)G_s(2,1)v_{xc}(2) = \int d2d3\, G_s(1,2)\Sigma[G_s](2,3)G_s(3,1). \tag{94}$$

In the simplest approximation, Σ is given by the exchange-only self-energy of Eq.(35),

$$\Sigma_x(1,2) = -\sum_j n_j\phi_j(1)\phi_j^*(2)w(1,2) \tag{95}$$

where n_j is the occupation number. This approximation leads to what is known as the time-dependent effective potential (TDOEP) equations [29, 30, 31] in the exchange-only approximation. Since the exchange self-energy Σ_x is local in time, there is only one time-integration in Eq. (94). The x-only solution for the potential will be denoted v_x. With the notation $\tilde{\Sigma}(3,4) = \Sigma_x(\mathbf{x}_3 t_3, \mathbf{x}_4 t_3) - \delta(\mathbf{x}_3 - \mathbf{x}_4) v_x(\mathbf{x}_3 t_3)$ we obtain from Eq.(94)

$$
\begin{aligned}
0 = & \, i \int_{t_0}^{t_1} dt_3 \int d\mathbf{x}_3 d\mathbf{x}_4 \, \left[G_s^<(1,3)\tilde{\Sigma}(3,4)G_s^>(4,1) - G_s^>(1,3)\tilde{\Sigma}(3,4)G_s^<(4,1) \right] \\
& + i \int_{t_0}^{t_0 - i\beta} dt_3 \int d\mathbf{x}_3 d\mathbf{x}_4 \, G_s^<(1,3)\tilde{\Sigma}(3,4)G_s^>(4,1). \qquad (96)
\end{aligned}
$$

Let us first work out the last term which describes a time-integral from t_0 to $t_0 - i\beta$. On this part of the contour we have $\phi_i(\mathbf{x}, t) = \phi_i(\mathbf{x}, t_0) \exp(-i\epsilon_i(t - t_0))$ and since Σ_x is time-independent on this part of the contour, we can integrate

$$
\begin{aligned}
& i \int_{t_0}^{t_0 - i\beta} dt_3 \, G_s^<(1,3)G_s^>(\mathbf{x}_4 t_3, 1) = \\
& \sum_{i,k} n_i(1 - n_k)\phi_i(1)\phi_i^*(\mathbf{x}_3, t_0)\phi_k(\mathbf{x}_4, t_0)\phi_k^*(1) \frac{e^{\beta(\epsilon_i - \epsilon_k)} - 1}{\epsilon_i - \epsilon_k} \qquad (97)
\end{aligned}
$$

If we then use $n_i(1 - n_k)(e^{\beta(\epsilon_i - \epsilon_k)} - 1) = n_k - n_i$ and define the function $u_{x,j}$ by

$$
u_{x,j}(1) = -\frac{1}{\phi_j^*(1)} \sum_k n_k \int d2 \, \phi_j^*(2)\phi_k(2)\phi_k^*(1) w(1,2) \qquad (98)
$$

we obtain from Eq.(97) and Eq.(95)

$$
\begin{aligned}
& i \int_{t_0}^{t_0 - i\beta} dt_3 \int d\mathbf{x}_3 d\mathbf{x}_4 \, G_s^<(1,3)\tilde{\Sigma}(3,4)G_s^>(4,1) \\
& = - \int d\mathbf{x}_2 \sum_j n_j \sum_{k \neq j} \frac{\phi_j^*(\mathbf{x}_2 t_0)\phi_k(\mathbf{x}_2 t_0)}{\epsilon_j - \epsilon_k} \phi_j(1)\phi_k^*(1) \left[u_{x,j}(\mathbf{x}_2 t_0) - v_x(\mathbf{x}_2 t_0) \right] + c.c. \qquad (99)
\end{aligned}
$$

The integral along the real axis on the lhs of Eq. (96) can similarly be evaluated. Collecting our results we obtain the OEP equations on the same form as in Ref. [31],

$$
\begin{aligned}
0 = & \, i \sum_j \sum_{k \neq j} n_j \int_{t_0}^{t_1} dt_2 \int d\mathbf{x}_2 \, \left[v_x(2) - u_{x,j}(2) \right] \phi_j(1)\phi_j^*(2)\phi_k^*(1)\phi_k(2) + c.c. \\
& + \sum_j \sum_{k \neq j} n_j \frac{\phi_j(1)\phi_k^*(1)}{\epsilon_j - \epsilon_k} \int d\mathbf{x}_2 \, \phi_j^*(\mathbf{x}_2, t_0) \left[v_x(\mathbf{x}_2 t_0) - u_{x,j}(\mathbf{x}_2 t_0) \right] \phi_k(\mathbf{x}_2, t_0). \qquad (100)
\end{aligned}
$$

Since the exchange-only self-energy Σ_x is Φ-derivable with respect to G_s, the potential v_x obtained from a solution of Eq.(100) will satisfy the zero-force constraint (90). The

OEP-equations (100) in the so-called KLI-approximation have been succesfully used by Ullrich et al.[30] to calculate properties of atoms in strong laser fields.
We finally note that one can readily extend our derivation to the case that we also have a vector potential present. In that case one obtains a similar TDOEP equation for the exchange-correlation part of the vector potential [32] which is a basic ingredient in current-density-functional theory [33, 34].

4. – Summary

We have given an overview of the Φ-formalism of Baym in connection with the Keldysh or time-contour Green function technique that describes nonequilibrium phenomena. We showed how Φ-derivability leads to satisfaction of conservation laws and that the Ward identities lead to gauge invariance conditions on the response functions and satisfaction of the f-sum rule. We further showed how the time-dependent exchange-correlation potential of time-dependent density-functional theory can be calculated from Green function techniques in such a way that this potential also satisfies important constraints that are enforced by the conservation laws. As an example we derived the exchange-only TDOEP equations. Much more on the relation between TDDFT and Green function techniques and on conserving approximations can be said but will be devoted to future publications.

APPENDIX A.

The frequency sum rule

Let us define the spectral function A by

$$A(\mathbf{r}_1,\mathbf{r}_2;t_1-t_2)=\chi^{>}_{00}(1,2)-\chi^{<}_{00}(1,2). \tag{A.1}$$

Eq.(70) is then equivalent to

$$\partial_t A(\mathbf{r}_1,\mathbf{r}_2;t)|_{t=0}=-\sum_{\mu}\nabla_{2,\mu}\nabla_{1,\mu}(n_0(\mathbf{r}_2)\delta(\mathbf{r}_1-\mathbf{r}_2)). \tag{A.2}$$

We will for convenience suppress the spatial indices. From Eq.(65) we further see that $A(t=0)=0$. The Fourier transform of A and its inverse are given by

$$\tilde{A}(\omega)=\int dt\, A(t)e^{i\omega t} \qquad A(t)=\int\frac{d\omega}{2\pi}\tilde{A}(\omega)e^{-i\omega t}. \tag{A.3}$$

From the second of these equations we immediately see that

$$A(t=0)=\frac{1}{2\pi}\int d\omega\,\tilde{A}(\omega) \qquad \partial_t A(t)|_{t=0}=\frac{-i}{2\pi}\int d\omega\,\omega\tilde{A}(\omega). \tag{A.4}$$

Now the Fourier transform of $\chi_{00,R}(t)$ is given by

$$\tilde{\chi}_{00,R}(\omega) = \int dt\, \theta(t) A(t) e^{i\omega t} \tag{A.5}$$

If we use the following representation of the theta-function

$$\theta(t) = \lim_{\eta \to 0} \frac{-1}{2\pi i} \int du \frac{e^{-iut}}{u + i\eta} \tag{A.6}$$

where η is positive, we can write

$$\tilde{\chi}_{00,R}(\omega) = \lim_{\eta \to 0} \frac{-1}{2\pi i} \int dt \int dv \frac{e^{ivt} A(t)}{\omega - v + i\eta} \tag{A.7}$$

From this equation we see that for large ω.

$$\tilde{\chi}_{00,R}(\omega) = \frac{-1}{2\pi i} \left(\frac{1}{\omega} \int dv \tilde{A}(v) + \frac{1}{\omega^2} \int dv\, v \tilde{A}(v) + O(1/\omega^3) \right) \tag{A.8}$$

However since $A(t = 0) = 0$ we obtain from Eq.(A.4) the following large frequency behavior for $\tilde{\chi}_{00,R}$

$$\tilde{\chi}_{00,R}(\omega) = -\frac{\partial_t A(t)|_{t=0}}{\omega^2} + O(1/\omega^3) \tag{A.9}$$

Since $\chi_{00,R}$ is causal, it is analytic in the upper half of the complex frequency plane and therefore a contour integral in the upper half plane will yield zero. If we let C be a semicircle in the upper half plane we find using Eq.(A.9)

$$0 = \int_C d\omega\, \omega \tilde{\chi}_{00,R}(\omega) = -i\pi \partial_t A(t)|_{t=0} + \int_{-\infty}^{+\infty} d\omega\, \omega \tilde{\chi}_{00,R}(\omega) \tag{A.10}$$

We therefore obtain

$$\int_{-\infty}^{+\infty} d\omega \omega \tilde{\chi}_{00,R}(\omega) = i\pi \partial_t A(t)|_{t=0} = -i\pi \sum_{\mu} \nabla_{2,\mu} \nabla_{1,\mu} (n_0(\mathbf{r}_2) \delta(\mathbf{r}_1 - \mathbf{r}_2)) \tag{A.11}$$

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